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FIRST ORDER QUADRUPOLE EFFECT IN DILUTE COPPER-BASED Cu-Zn ALLOYS

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BUDAPEST

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Summary

The wipe-out number for the first order quadrupole effect was evaluated from the measured concentration dependence of ^{63}Cu NMR lines in dilute Cu-Zn alloys with Zn content varying from 300 to 2100 ppm, as n_s=490. A quantitative interpretation of this result is given by making use of Friedel's theory and the Alfred-Van Ostenburg's phase shifts indicating virtual p-electron scattering.

The aim of our investigations is to get a better insight into the asymptotic behaviour of the excess conduction electron charge density around impurities in dilute copper-based alloys. The information source is the first order quadrupole effect of the ^{63}Cu NMR spectrum [1]. This effect, which is proportional to the component z of the electric field gradient /q/, has a substantially longer range extending over matrix nuclei lying much farther from the impurity, as compared with the second order quadrupole effect, proportional to q^2. It is expected therefore that the results will be less affected by the preasymptotic behaviour than in the case of the second order effect.

The earlier measurements [2] of the signal width in dilute Cu-Pt alloys have shown the ranges of the two effects to be well separable. A similar observation was made on the Cu-Zn system. The present report is restricted to the range of the first order quadrupole effect.

The alloys were prepared from 99,998 at% purity Cu and 99,95 at% purity Zn by induction smelting under argon atmosphere in a graphite crucible. The master alloy containing 12,5 at% of Zn was diluted to Zn concentrations of 0,031$\pm$0,002; 0,102$\pm$0,005; 0,214$\pm$0,009 at%, as determined by spectrographic analysis [3].

Foils of $\sim 20\mu$ thickness were produced by cold rolling and subsequent annealing under 80 % argon + 20 % hydrogen atmosphere at 500°C for 6 hours [4]. The rolling was performed in a manner to obtain possibly isotropic crystallite orientation. The NMR data showed an anisotropy of a few percents, the reported values are averages taken over spectra measured in different directions. For reference pure copper /99,999 at% purity Johnson - Matthey/, as marker signal ^{27}Al NMR in Alfoils, measured simultameously with the alloy, were used. The experimental accuracy was the same as that reported in [2]. The measurements were performed at a frequency of 6 MHz and at room temperature.

The experimental data are presented in Fig. 1 where the plot for satellite intensity vs Zn concentration is shown. The logarithm of the intensity is seen to vary, within the experimental error, linearly with the Zn concentration, the slope of the curve n_s=490.

In the interpretation of the experimental results only the soattering by the impurity atoms is taken into account. The Beal-Monod Kohn--type scattering by displaced matrix atoms [5] is of no importance in dilute Cu-Zn and also the "size effect" described by Sagalyn et al. [6] can be ignored, since, as observed in our direct measurement [7], the value of the empirical parameter λ is less than 1,5.

The asymptotic form of the field gradient is expressed [8] as

$$q(r) = \frac{8\pi}{3}\,\alpha\,\Delta\rho(r)\ ;\quad \Delta\rho(r) = A\,r^{-3}\cos(2k_F\,r + \varphi)$$

The enhancement factor α was estimated by [8] for copper as 25,6. The amplitude A and the phase φ, characterizing the excess electron density, as defined by [8], are determined exclusively by the phase shifts of the scattered partial waves taken at the Fermi energy. The value of the field gradient is uniquely determined by the phase shifts. Several methods are available for their evaluation.

From the best known methods we mention that of Blatt [9] (B). Blatt assumes a square-well potential for the solute atoms. He determined the depth of the well from the modified Friedel sum rule and its width in an arbitrary manner. He interpreted the residual resistivity of Cu and Ag base alloys with their help. His results for Cu-Zn alloys are shown in Table 1.

Kohn and Vosko [8] (KV) derived semiempirically two phase shifts /assumed to be prevailing/ from the measured residual resistivity and the Friedel sum rule. They explained the second order quadrupole effects of

the Cu base dilute alloys by the phase shifts determined in this way; the agreement is qualitative.

The scheme of Alfred and Van Ostenburg [10] (AVO) generates phase shifts of unlimited order utilizing the residual resistivity, the Friedel sum rule and a generalized free-electron potential. The Knight shift of Cu and Ag base dilute alloys is in quantitative agreement with the results obtained.

In these methods the deformation of the crystal lattice around the impurity is considered as $E' = Z - \frac{\Delta V}{\Omega}$ the variation of the screened charge [9], where Z is the difference in the valence of the impurity and the matrix atoms and $\Delta V/\Omega$ is the relative change of size of the cell occupied by the impurity.

We mention further the results of Langer and Vosko [11] (LV) using many-body perturbation theory.

Table 1 shows the phase shifts, oscillation amplitudes and phase factors calculated on the basis of the different methods. In the lines 1., 2. and 3. the solutions obtained by the mehtods of Blatt, Kohn-Vosko and Alfred Van Ostenburg respectively, and in line 4 the values obtained by the Langer-Vosko method are shown.

In principle, the NMR spectrum can be predicted, if the value of the field gradient is known and one assumes first order quadrupole effect [12]. In this case the spectrum can be computed at a given impurity concentration for every possible matrix-impurity configuration and the resultant spectrum is given by the sum of the contributions weighted with the occurrence probability of the configurations. Actually, this evaluation is impracticable, thus one uses simplifying approximations for the description of the experimental data. The most simple is to compare, if there are any, some exclusively effect dependent in our case, quadrupole effect dependent parameters of the measured and the theoretical spectrum. The slope of the logarithmic intensity vs concentration curve can be considered such a parameter determined within experimental error by the first order quadrupole effect.

The experimental wipe-out number was compared with the predictions from two models. In either case the perturbation was assumed to be due to a single impurity. Both models work better, for lower impurity concentrations and smaller amplitudes of the charge density oscillations.

a./ The "all or nothing" model /see e.g. [8]/. The theoretical value of n_s is a function of the arbitrarily chosen parameter q_{crit}.

Taking for Cu-Zn alloys $q_{crit}=1,8.10^{21}cm^{-3}$, the experimental wipeout number is the same as that obtained in terms of the "all or nothing" model with $A=1,6.6^{-2}$ and $\varphi=23,5^{o}$ and this value of q_{crit} is not unreasonable physically.

b/ Taking into account the angular dependence of the quadrupole interaction and the dipole-dipole broadening of the spectrum [6] we can give w(qr) the contribution of a matrix nucleus seen by the field gradient qr to the wipe-out number as,

$$w(qr) = 1 - \int_{o}^{\infty} p_{qr}(\nu)\, f(\nu - \nu_o)\, d\nu$$

where qr is the field gradient in dimensionless units, p_{qr} /ν/ is the first order quadrupole spectrum of the polycrystalline sample [11].
$\int_{o}^{\infty} p_{qr}(\nu)\, d\nu = 1$, $f/\nu - \nu_o/$ is the contribution to the derivative spectrum from dipole-dipole interaction, normalised as $f(\nu_o)= 1$. /calculating $w/q_r/$ it is the experimental spectrum of pure copper or a Gaussian curve, the two results are hardly different/.

The wipeout number is given as

$$n_s = \sum_{i=1}^{N} w(q_{ri})\, n_i \quad ,$$

Where n_i is the number of nuclei in the ith coordination shell. The summation was performed by an ICT - 1900 computer over 400 coordination shells /see Figure 2 and Figure 3/ and the result was found to be hardly dependent on ϕ .

Taking the enhancement factor $\alpha = 25$, with measured wipeout number the model yields for the charge density oscillation amplitude $A = 1,6.10^{-2}$. Considering the given uncertainties, the agreement with Alfred's van Ostenburg's phase shifts is surprisingly good. The phase shifts reported in the literature yield, as a rule, a larger amplitude as compared with the measurement eg. with the Kohn Vosko's phase shifts [8] it is 70 %.

The field gradient calculated from the present results for a few neighbours is lower than evaluated from the measurements of the second order effect [12], [8] and [6] and if the asymptotic behaviour holds in the case of second and third neighbours, the field gradient must be considerably lower than the value obtained by Redfield [13] from pure quadrupole resonance experiments.

Acknowledgments

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Table I.

Phase shifts and excess conduction electron charge density parameters in Cu-Zn dilute alloys

	η_0	η_1	η_2	η_3	A	φ
B	0,5319	0,241	0,0277		0,00749	-37°
KV	0,521	0,35	-	-	0,02755	$+11,1^\circ$
AVO*	0,203	0,254	0,059	0,014	0,01625	$23,25^\circ$
LV	-	-	-	-	0,0236	180°

* $\eta_4 = 0,004$

Figure captions

Fig. 1 ^{63}Cu NMR satellite intensity vs Zn concentration in copper based Cu-Zn dilute alloys.

Fig. 2 The contribution of a matrix nucleus seen by the field gradient q_r to the wipe our number W $/q_r/$.

Fig. 3 Satellite wipeout number vs. excess charge density oscillation amplitude.

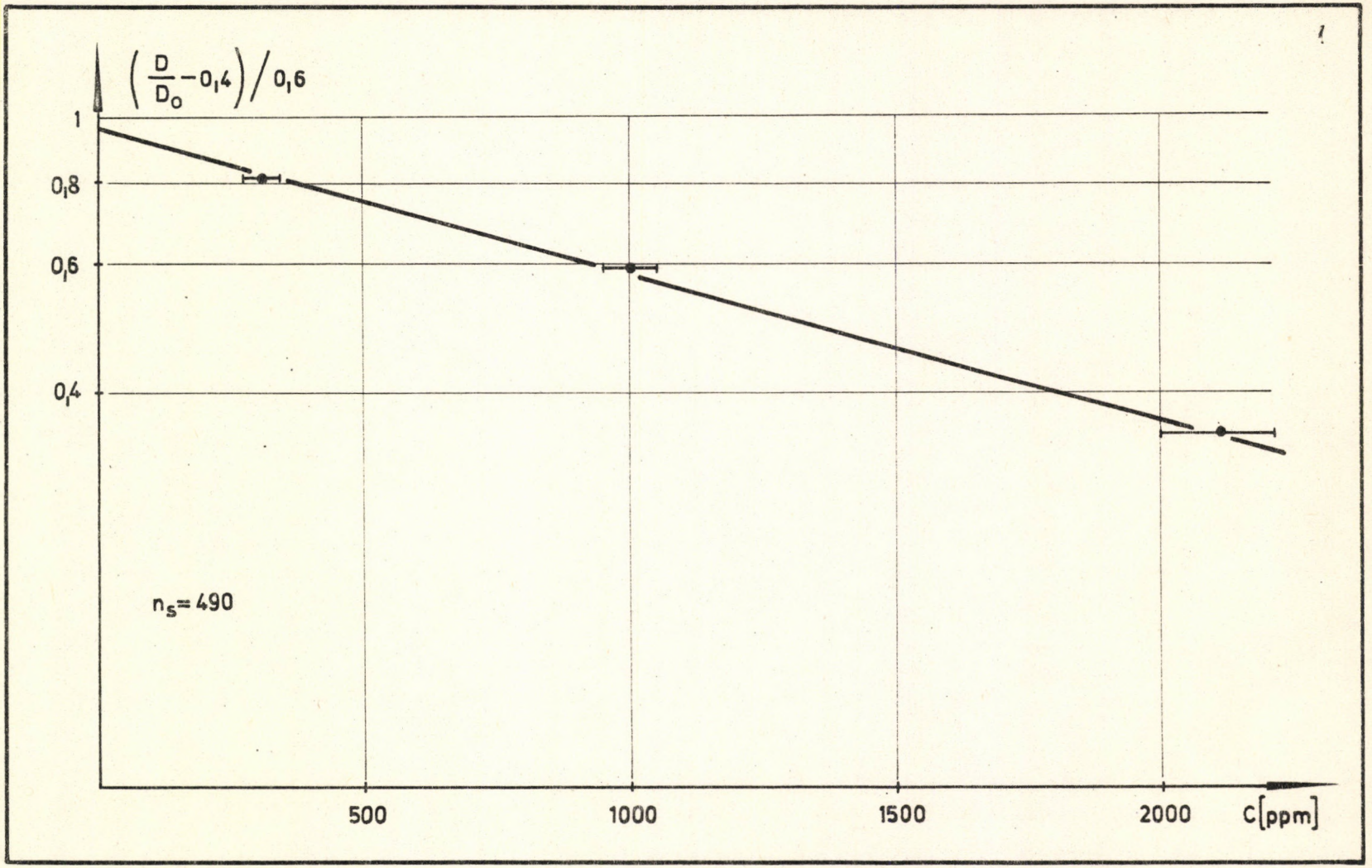
$\left(\frac{D}{D_o}-0{,}4\right)/0{,}6$
1
0,8
0,6
0,4
$n_s = 490$
500
1000
1500
2000
C[ppm]

Fig. 1

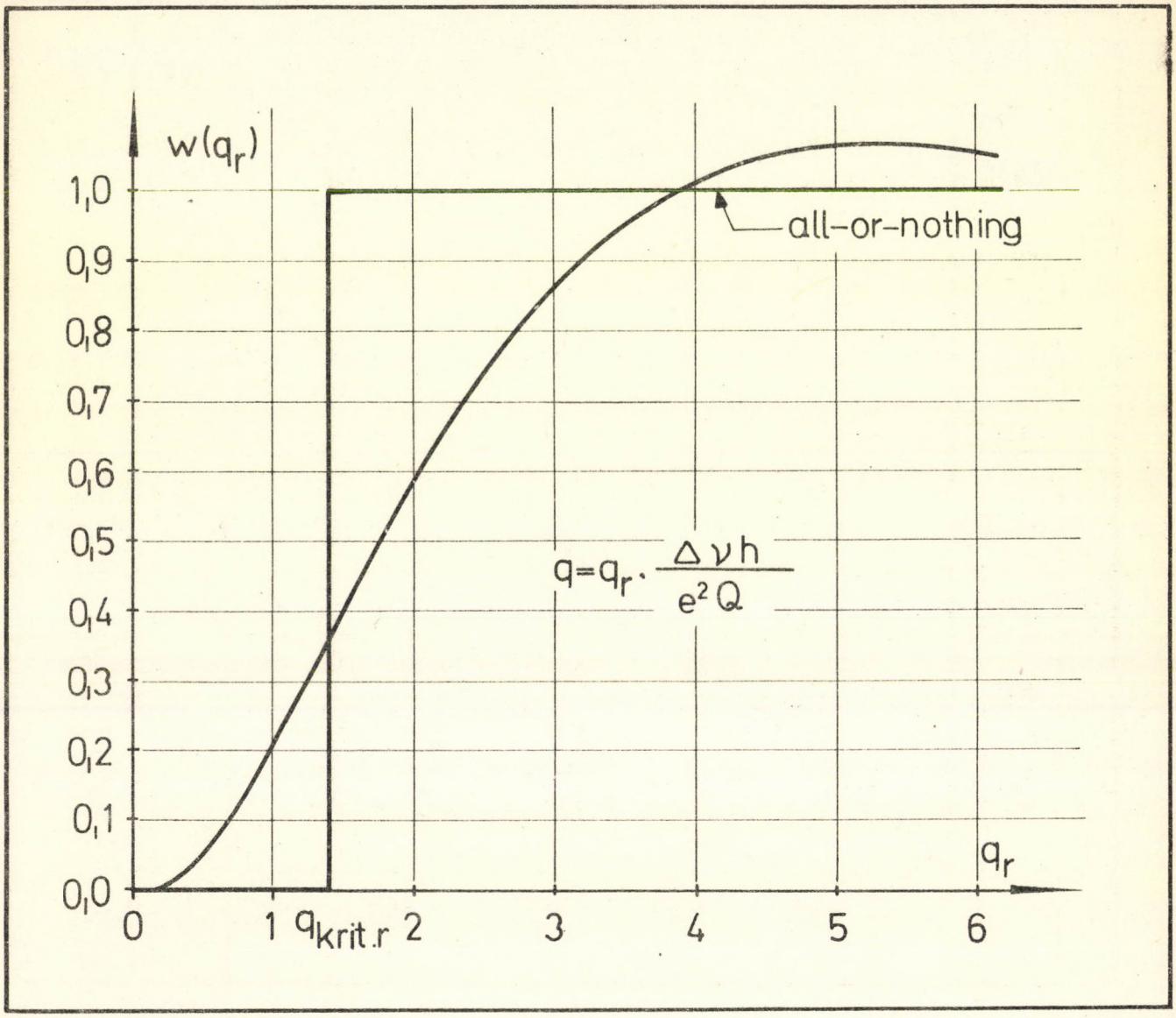
w(q_r)
1,0
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0,0
0
1 q_krit.r
2
3
4
5
6
q_r
all-or-nothing
q=q_r · Δνh / e²Q

Fig. 2

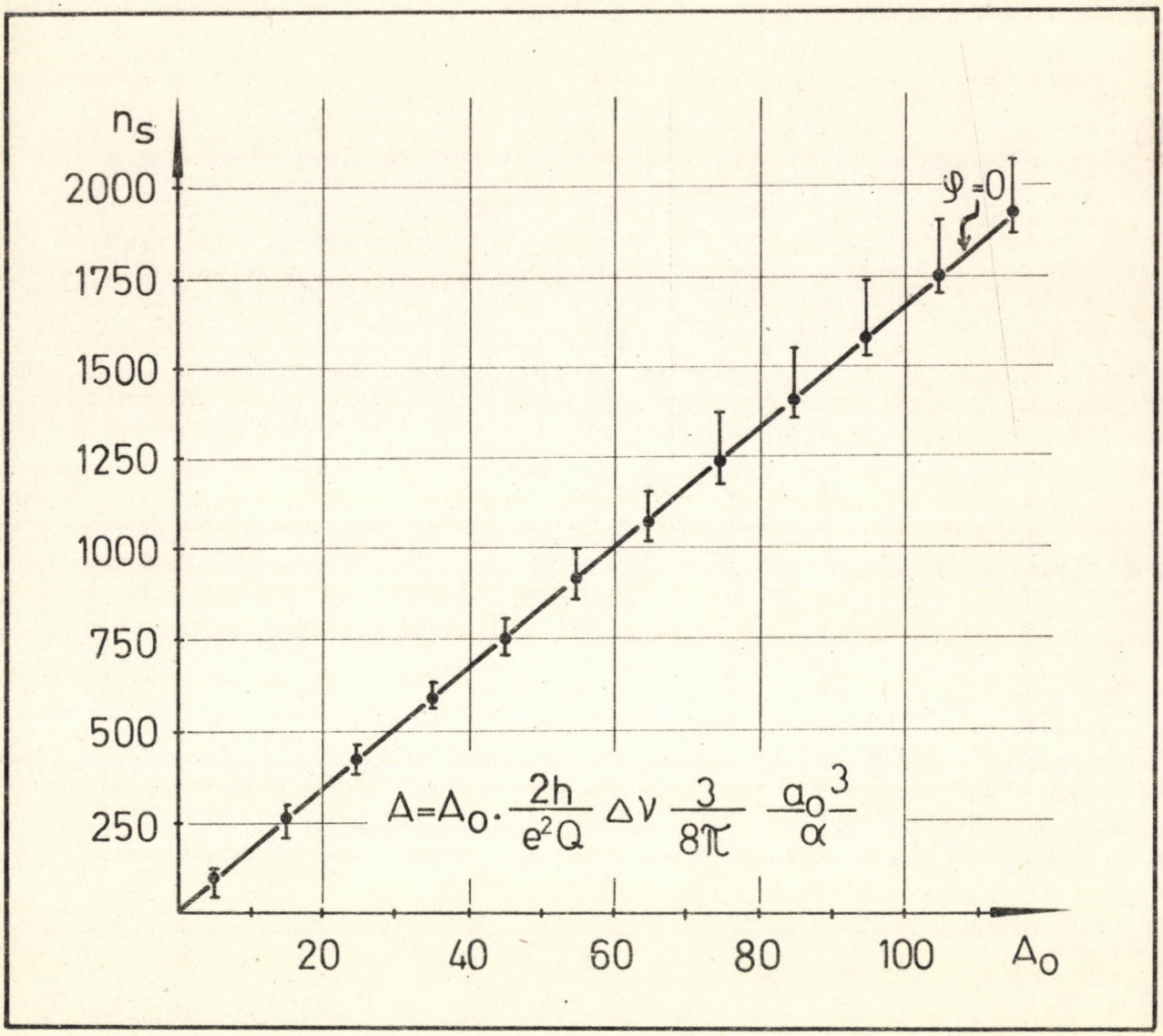
n_s
2000
1750
1500
1250
1000
750
500
250
$\varphi = 0$
$A = A_0 \cdot \frac{2h}{e^2 Q} \Delta\nu \frac{3}{8\pi} \frac{a_0^3}{\alpha}$
20
40
60
80
100
A_0

Fig. 3

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